

# Chemistry of Epoxy Compounds. IX.<sup>2</sup> Epoxidation of Oleamide and N-Substituted Oleamides with Peracetic Acid

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Previous papers in this series,<sup>3,4</sup> reported the epoxidation of mono-unsaturated fatty acids, esters and hydrocarbons, as well as oleyl alcohol and some triglycerides, with peracetic acid in acetic acid solution. In these papers, it was shown that, contrary to the generally accepted idea, peracetic acid in acetic acid solution could be employed for the preparation of oxirane ( $\alpha$ -epoxy) compounds in good yield from unsaturated compounds. Thus, it was demonstrated that peracetic acid behaved in exactly the same manner as perbenzoic or monoperphthalic acid, although admittedly yields of oxirane compounds were sometimes lower than would be anticipated if the aromatic peracids had been employed. The ease with which an acetic acid solution of peracetic acid can be prepared from readily available starting materials,<sup>3,5</sup> however, makes it an attractive epoxidizing reagent.

This investigation was initiated for a dual purpose. First, we wished to demonstrate that long-chain unsaturated amides could be successfully epoxidized, thus adding to the classes of compounds epoxidizable by peracetic acid and further substantiating the hypothesis regarding

available and those which have been reported in the literature have relatively limited chemical reactivity, and we wished to prepare long-chain compounds which not only retained the amide group but also contained an extremely reactive functional group. The presence of the reactive oxirane group in a long-chain amide suggests many interesting reactions leading to the formation of potentially valuable products.

In this study, oleamide and N-substituted oleamides<sup>6</sup> have been converted to the corresponding 9,10-epoxystearamides in 30-90% yield by epoxidation with peracetic acid in acetic acid solution. The reaction proceeded smoothly and rapidly at 20-30° with a 20% molar excess of peracetic acid; approximately four hours reaction time was required. After an analysis indicated that no more peracetic acid was being consumed, the reaction mixtures were poured into cold water, and the crude epoxystearamides were separated by filtration and purified by recrystallization from organic solvents. The pure compounds were white, crystalline solids, insoluble in water and cold organic solvents, but readily soluble in hot organic solvents. The results are summarized in Table I.

TABLE I  
CHARACTERISTICS OF 9,10-EPOXYSTEARAMIDES  $\text{CH}_3-(\text{CH}_2)_7-\text{CH}-\text{CH}-(\text{CH}_2)_7-\text{CONHR}$

R	Crude amides			Purified amides								
	Yield, %	Oxirane oxygen, %	M. p., °C.	Yield, %	M. p., °C.	Carbon, % Calcd. Found	Hydrogen, % Calcd. Found	Nitrogen, % Calcd. Found	Oxirane oxygen, % Calcd. Found	Oxirane oxygen, % Calcd. Found	Oxirane oxygen, % Calcd. Found	Oxirane oxygen, % Calcd. Found
Hydrogen	98	4.54	90.0-90.5	65 <sup>b</sup>	94.0	72.7 72.7	11.9 11.5	4.71 4.54	5.38 5.28	5.38 5.28	5.38 5.28	5.38 5.28
Methyl	98	4.49	64.0-65.0	38 <sup>b</sup>	65.5-66.0	73.3 73.3	12.0 12.3	4.50 4.43	5.14 5.20	5.14 5.20	5.14 5.20	5.14 5.20
n-Hexyl	98	3.53	62.0-63.5	53 <sup>b</sup>	66.0-66.5	75.5 75.8	12.4 12.7	3.67 3.58	4.19 4.14	4.19 4.14	4.19 4.14	4.19 4.14
n-Decyl	99	3.21	73.0-73.5	89 <sup>c</sup>	75.0-75.5	76.8 77.2	12.7 12.7	3.21 3.18	3.66 3.51	3.66 3.51	3.66 3.51	3.66 3.51
n-Dodecyl	98	2.80	75.5-76.0	45 <sup>b</sup>	78.5-79.0	77.4 77.3	12.8 12.7	3.01 2.92	3.44 3.36	3.44 3.36	3.44 3.36	3.44 3.36
Phenyl	99	3.73	80.0-81.0	45 <sup>d</sup>	83.0-83.5	77.2 77.1	10.5 10.3	3.75 3.75	4.28 4.28	4.28 4.28	4.28 4.28	4.28 4.28
2-Hydroxyethyl	97	4.20	79.0-80.0	50 <sup>e</sup>	81.5-82.0	70.3 70.3	11.5 11.6	4.11 3.99	4.68 4.65	4.68 4.65	4.68 4.65	4.68 4.65
Acetyl	99	3.92	71.0-72.0	29 <sup>f</sup>	74.0-75.0	70.8 70.8	11.0 11.0	4.12 4.07	4.71 4.51	4.71 4.51	4.71 4.51	4.71 4.51

\* Determined by the method of Swern, Findley, Billen and Scanlan, *Anal. Chem.*, 19, 414 (1947). <sup>b</sup> Crystallized two to four times from acetone, 7 to 10 ml./g., at 25°. <sup>c</sup> Crystallized as in <sup>b</sup>. Further crystallization from 95% ethanol, 3 ml./g. and 12 ml./g. at 25°, did not increase the purity as determined by the % oxirane oxygen. <sup>d</sup> Crystallized twice from petroleum naphtha, boiling range 63-70°, 5 ml./g. at 23°, and twice from acetone, 6 ml./g. at 25°. <sup>e</sup> Crystallized three times from 95% ethanol, 5 ml./g. at 0°. <sup>f</sup> Crystallized four times from acetone, 4 ml./g. at 0°, and twice from 95% ethanol, 2 ml./g. at 25°. Further crystallization from ethanol did not increase the purity as determined by the % oxirane oxygen.

the generality of this reaction.<sup>3</sup> Second, most of the long-chain amides which are commercially

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(2) For paper VIII of this series, see *THIS JOURNAL*, 71, 1152 (1949).

(3) Findley, Swern and Scanlan, *ibid.*, 67, 412 (1945).

(4) Swern, Billen and Scanlan, *ibid.*, 68, 1504 (1946).

(5) Swern, *Chem. Rev.*, in press (1949).

## Experimental

**Materials Used.**—Oleamide and N-substituted oleamides were prepared as described in an earlier paper.<sup>6</sup> Peracetic acid was prepared by the procedure of Findley, Swern and Scanlan.<sup>3</sup>

**Epoxidation Techniques.**—Since the epoxidation procedure is substantially the same for each of the amides, details will be given for the preparation of N-(n-hexyl)-

(6) Roe, Scanlan and Swern, *THIS JOURNAL*, 71, 2215 (1949).

9,10-epoxystearamide only. To a well-stirred solution of 18.3 g. (0.05 mole) of N-(*n*-hexyl)-oleamide<sup>6</sup> (iodine number, 69.3; m. p. 31.0–31.5°) in 10 ml. of glacial acetic acid at 20°, 55 ml. of approximately 1 *M* peracetic acid solution<sup>7</sup> (0.06 mole) was added within five minutes. The reaction temperature was maintained between 20 and 25° by external cooling, and a peroxide oxygen analysis was run at hourly intervals.<sup>7</sup> After about four hours, 85–90% of the calculated quantity of peracetic acid had been consumed, and the reaction mixture was then poured into about 500 ml. of ice-water. A granular solid precipitated, which was filtered off and washed with several portions of cold water. After being air-dried, the crude N-(*n*-hexyl)-9,10-epoxystearamide (purity, about 84%), m. p. 62–63.5°, weighed 18.6 g. Recrystallization to constant melting point from acetone at 25° resulted in a 53% yield of pure N-(*n*-hexyl)-9,10-epoxystearamide, m. p. 66.0–66.5°.

The quantity of glacial acetic acid required to dissolve 0.05 mole of the unsaturated amide varied with the amide employed, and was just sufficient to give a homogeneous solution at 20–25°. N-(*n*-Decyl)-oleamide required 840 ml. of glacial acetic acid. N-(*n*-Dodecyl)-oleamide was

too insoluble in acetic acid at 20–25°; it was dissolved in 200 ml. of acetic acid at 30°, and the epoxidation reaction was conducted at that temperature. Higher temperatures should be avoided because of the increased rate of decomposition of peracetic acid and also because of the increased rate at which the oxirane ring is opened by acetic acid.

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#### Summary

Peracetic acid in acetic acid solution has been used to epoxidize some long-chain mono-unsaturated amides. 9,10-Epoxystearamide and a series of N-substituted 9,10-epoxystearamides have been prepared in 30–90% yield by the epoxidation of oleamide and N-substituted oleamides.

(7) Wheeler, *Oil and Soap*, **9**, 89 (1932).